

# The High Magnetic Field Phase Diagram of a Quasi-One Dimensional Metal

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## Abstract

We present a unique high magnetic field phase of the quasi-one dimensional organic conductor  $(\text{TMTSF})_2\text{ClO}_4$ . This phase, termed "Q- $\text{ClO}_4$ ", is obtained by rapid thermal quenching to avoid ordering of the  $\text{ClO}_4$  anion. The magnetic field dependent phase of Q- $\text{ClO}_4$  is distinctly different from that in the extensively studied annealed material. Q- $\text{ClO}_4$  exhibits a spin density wave (SDW) transition at  $\approx 5$  K which is strongly magnetic field dependent. This dependence is well described by the theoretical treatment of Bjelis and Maki. We show that Q- $\text{ClO}_4$  provides a new B-T phase diagram in the hierarchy of low-dimensional organic metals (one-dimensional towards two-dimensional), and describe the temperature dependence of the of the quantum oscillations observed in the SDW phase.

Quasi-one dimensional organic metals have the general character of a large bandwidth along the molecular stacking (chain) direction, followed by significantly smaller band widths in the inter-chain and inter-plane directions<sup>1</sup>. For the Bechgaard salts these ratios are ( $t_a$ ,  $t_b$ ,  $t_c$ : 1000, 250, 3 meV) respectively<sup>2</sup>. For sufficiently small transverse bandwidths, a one-dimensional conductor will undergo an instability, at a critical temperature, to an insulating ground state. Following Yamaji<sup>3</sup>, this temperature has an anisotropic bandwidth dependence in terms of the so called "imperfect nesting parameter",  $\varepsilon_0 = t_b^2/t_a$ . Hence the more two-dimensional the material is, the larger  $\varepsilon_0$  will be, and the lower the temperature where the instability, or "nesting" will occur. In the case of the Bechgaard salts, a spin density wave (SDW) ground state is formed. For sufficiently large  $\varepsilon_0$ , the low temperature ground state remains metallic, but high magnetic fields can effectively reduce  $\varepsilon_0$  (i.e. drive the system more one-dimensional), and a field induced spin density wave state (FISDW) can be stabilized<sup>4</sup>. This latter phenomena has been the subject of extensive experimental and theoretical work<sup>1</sup>.

In this communication we consider a system where  $\varepsilon_0$  is large, but where an SDW state still forms at a temperature  $T_{SDW} = 5$  K. This allows a unique situation where  $T_{SDW}$  increases by a factor of two in high magnetic fields due to the close competition between  $\varepsilon_0$  and the magnetic energy. To accomplish this we employ the well-studied organic conductor (TMTSF)<sub>2</sub>ClO<sub>4</sub>.<sup>1</sup> What is particular to our approach is that the material has been prepared in a very rapidly (30K/sec) thermally quenched state (i.e. Q-ClO<sub>4</sub>) to preserve the high temperature electronic structure, which is comprised of two, open orbit, warped Fermi surface sheets. Otherwise, if the material is slowly cooled, the tetrahedral anion ClO<sub>4</sub> undergoes an ordering transition around 24 K, the unit cell doubles in the b direction, and the resulting Fermi surface becomes more complex<sup>5</sup>. Generally, it is this relaxed state of the material (hereafter R-ClO<sub>4</sub>), which has been most extensively studied. In contrast, Q-ClO<sub>4</sub> is in the class of Bechgaard salts<sup>2</sup> (TMTSF)<sub>2</sub>X where X = PF<sub>6</sub>, AsF<sub>6</sub>, NO<sub>3</sub> which form an SDW state at ambient pressure below a transition temperature  $T_{SDW}$  (12 K for X = PF<sub>6</sub> and AsF<sub>6</sub>, 10K for X = NO<sub>3</sub>, and 5 K for X = Q-ClO<sub>4</sub>). In these cases a high magnetic

field improves the nesting condition<sup>6,7,11</sup>, and  $T_{SDW}$  increases with magnetic field. We have determined that not only does this happen for the case of Q-ClO<sub>4</sub>, but the effect is the most dramatic, and leads to a new phase diagram in the hierarchy of nesting parameters ( $7\text{ K} \leq \varepsilon_0 \leq 22.5\text{ K}$ ) in the Bechgaard salts.

The measurements reported here were carried out on two samples in 50 T (sample #1) and 60 T (sample #2) pulsed-field magnets at the Los Alamos National Laboratory. Electrical transport contacts were made via graphite paint and  $12\mu\text{m}$  gold wires, with a dc four-terminal technique with a current of  $50\text{ }\mu\text{A}$ . The current was applied transverse to the layers along the c-axis, as were the voltage contacts. The magnetic field is also along the c-axis. To ensure that the samples fully quenched, the samples were put in direct contact with liquid helium from room temperature as rapidly as possible. Estimated cooling rates were of order 30 K/sec or greater. The use of graphite paint appeared to greatly enhance the reliability of the contacts and to reduce degradation (cracking) of the samples during the rapid cool-downs. Systematic temperature measurements for each run were performed with a single quench to preserve the anion disorder in the samples.

In Fig. 1a we show a summary of the magnetoresistance measurements for sample #1 above 5 K, and in Fig. 1b similar measurements at lower temperatures for both samples #1 and #2 are presented. In the inset of Fig. 1a the temperature dependence of the c-axis resistivity is shown at zero magnetic field. Here the upturn is the onset of the spin density wave transition, as established by, for instance NMR studies<sup>9</sup>. In Fig. 2 we show an expanded view of the behavior of the magnetic field dependent resistance, where the data has been plotted vs. the square of the magnetic field. All data shown is for temperatures higher than  $T_{SDW}$  ( $B=0$ ). Here the magnetoresistance remains small, and quadratic in field, until a critical field (hereafter  $B_{SDW}$ ) is reached. We have fit the 10.6 K resistance data in Fig. 2 to the quadratic function (expected for the case of an open orbit metal) below the point where the slope changes. Aside from a weak temperature dependence, all of the data follow this general functional dependence until the point  $B_{SDW}$  is reached.  $B_{SDW}$  is temperature dependent, and is manifested as a change in the field dependence

of the magnetoresistance. This defines the threshold field between the metallic and SDW ground states. Above  $B_{SDW}$ , additional structure appears (hereafter  $B'_{SDW}$ ) where the field dependence of the magnetoresistance changes again. At higher fields quantum oscillations of frequency  $F=190$  T become evident. We will return to these last two points in the discussion below.

In Fig. 3 we summarize the dependence of  $B_{SDW}$  and  $B^*$  in terms of the corresponding temperatures  $T_{SDW}$  and  $T^*$  based on the analysis of Fig. 2 and the zero field value from the inset of Fig. 1a. The new phase diagram, as defined by Fig. 3, is the main result of the present work. To put the new data for Q-ClO<sub>4</sub> in perspective, we have included previous results for AsF<sub>6</sub>, PF<sub>6</sub>, and NO<sub>3</sub>, (Refs.<sup>7,6,8</sup>) for the field dependence of  $T_{SDW}$  in terms of the theoretical framework, which describes the magnetic field dependence of  $T_{SDW}$  as given by Bjelis and Maki in the form<sup>10</sup>

$$\ln \left[ \frac{T_{SDW}}{T_{SDW0}} \right] \cong \sum_{l=-\infty}^{\infty} J_l^2(e_0) \left\{ \text{Re} \Psi \left( \frac{1}{2} + 2ilx_1 \right) - \Psi \left( \frac{1}{2} \right) \right\}. \quad (1)$$

Here  $e_0 = \varepsilon_0 / \omega_b$ , where  $\varepsilon_0$  is the imperfect nesting parameter described above, and  $\omega_b = ev_F b B$ . The latter is the effective cyclotron frequency along the b-axis, where  $v_F$  is the Fermi velocity.  $J_l$  and  $\Psi$  are Bessel and digamma functions respectively, and  $x_1 = \omega_b / 4\pi T_{SDW}$ .  $T_{SDW0}$  corresponds to the transition temperature for perfect nesting. This expression, in an asymptotic form<sup>6</sup>, successfully describes the field dependence of  $T_{SDW}$  for (TMTSF)<sub>2</sub>NO<sub>3</sub> Ref.<sup>6</sup> and (TMTSF)<sub>2</sub>PF<sub>6</sub> Ref.<sup>11</sup>. For Q-ClO<sub>4</sub>, Eq. 1 is also applied, but its full (non-asymptotic) form must be used to obtain proper convergence at low magnetic fields due to the large imperfect nesting parameter  $\varepsilon_0$  needed to describe the data. (The fitting parameters for all three materials are listed in the caption of Fig. 3.) It is clear that  $T_{SDW}(B=0)$  decreases with increasing  $\varepsilon_0$ . However, since the general Fermi surface topology is very similar, all three materials approach a common transition temperature in the high field limit.

For completeness, the phase diagram of R-ClO<sub>4</sub> is also shown<sup>5</sup> in Fig. 3. A point that must be clearly made is that the Q-ClO<sub>4</sub> phase diagram is very different from that studied in the R-ClO<sub>4</sub> case. For R-ClO<sub>4</sub> the Fermi surface topology involves double open orbit

sheets due to the anion ordering, the imperfect nesting is so large that at zero field the system is metallic, even superconducting ( $T_c = 1.2$  K), and the maximum field induced  $T_{SDW}$  is less than 6 K. Another factor which distinguishes Q-ClO<sub>4</sub> from R-ClO<sub>4</sub> is that the quantum oscillation frequency in the magnetoresistance is 190 T, as confirmed by this (see below) and previous independent studies<sup>11</sup>. In contrast, for R-ClO<sub>4</sub> the frequency is 250 T. This confirms that the Fermi surface topologies are fundamentally different. Returning for a moment to the observation of the  $B'_{SDW}$  feature (Figs. 2 and 3), it is not clear what assignment to make to it (i.e. a SDW sub-phase for instance). It falls outside the prediction of Eq. 1 since there only one transition ( $B_{SDW}$ ) is predicted. Hence further experimental and theoretical work will be needed to fully understand the significance of  $B'_{SDW}$ .

We next turn to the nature of the oscillations in the magnetoresistance which appear above  $B_{SDW}$  (see Fig. 1). The oscillatory component of the magnetoresistance, plotted as  $\Delta R/R$  vs. inverse magnetic field is shown in Fig. 4a and 4b for representative temperatures. (Here R is the non-oscillatory background magnetoresistance.) The oscillation amplitude increases until about 5 K, but then rapidly vanishes at lower temperatures. In Fig. 4c we show the amplitude of the oscillations (normalized by R ) as a function of temperature. Such oscillations, commonly called "rapid oscillations" or "RO" appear in a number of the quasi-one dimensional organic salts, including the Bechgaard salts<sup>1</sup> and the (DMET-TSeF)<sub>2</sub>AuCl<sub>2</sub> salts<sup>12</sup>. These oscillations are periodic in inverse field, with a frequency of between 190 and 250 T. If considered as closed orbits, they represent about 3% of the first Brillouin zone. A general observation is that they only occur when the original open orbit Fermi surface has undergone a reconstruction. This can happen by an anion ordering transition<sup>13</sup> and/or nesting of the Fermi surface<sup>11</sup>. In many cases where a spin density wave ground state is stabilized, the amplitude of the rapid oscillations first increases with decreasing temperature, but below a characteristic temperature  $T^*$  (typically between 2 to 4K), the amplitude attenuates exponentially for  $T \rightarrow 0$ . These oscillations have been described as a magnetic breakdown phenomena<sup>11</sup> in an imperfectly nested Fermi surface topology. However, below  $T^*$  there is an improvement of the nesting condition, such that

more of the reconstructed Fermi surface becomes gapped, and the magnetic breakdown becomes less probable. As shown in Fig. 4c, and following Ref.<sup>11</sup>, this behavior may be modeled by the standard Lifshitz - Kosevich description for quantum oscillations above  $T^*$ , and an exponential attenuation below  $T^*$ . Here the parameters of the model involve an effective mass  $m^* = 1.2 m_0$ , a Dingle temperature  $T_D = 7$  K, a  $T^* = 3.75$  K, and a low temperature magnetic breakdown gap of 10 K.

The Dingle temperature associated with the quantum oscillations discussed above gives insight into the nature of carrier scattering, and therefore disorder, in Q-ClO<sub>4</sub>. Typically for "clean" organic metals where strong quantum oscillations are observed<sup>14</sup>,  $T_D$  is of order 1 K. For Q-ClO<sub>4</sub> it is considerably higher ( 7 K). Since anion disorder is necessary to stabilize the Q-ClO<sub>4</sub> state, this could be a possible source for the enhanced scattering. However, similar studies of the quantum oscillations in AsF<sub>6</sub> and PF<sub>6</sub> anion systems<sup>11</sup>, where there is no disorder involved, show a similar value of  $T_D$ . Furthermore, given that the SDW state, which should be sensitive to disorder, readily develops in Q-ClO<sub>4</sub>, we speculate that in spite of the anion disorder, the material is in some sense still relatively clean, and the large value of  $T_D$  may be characteristic of the SDW (antiferromagnetic ) nature of these systems.

One other feature of the low temperature data is shown in Fig. 1b. Below about 3 K there are two distinct changes (shown by the arrows) in the magnetoresistance, one at around 12 T, and the other around 30 T. At present we have no explanation for these features. One possibility is that this behavior is related to the  $T^*$  mechanism in some manner. Another is that these changes are some vestige of the anion-ordered state that only shows up when the resistivity of the predominantly quenched state is sufficiently high. (The characteristic fields are close to some of the major FISDW phase boundaries in the R-ClO<sub>4</sub> compound<sup>15</sup>.)

In summary, the present work shows the evolution of the metal-to-spin density wave transition for open orbit, quasi-one dimensional metals with changes in their nesting parameters. By mapping the magnetic field dependence of the spin-density wave transition, we provide a description of a new field dependent ground state of the material (TMTSF)<sub>2</sub>ClO<sub>4</sub>

where its low temperature anion ordering transition has been suppressed. The theory of Bjelis and Maki provide an excellent framework to describe the general field dependent features of these systems. New aspects of the  $\text{Q-ClO}_4$  ground state include the full description of the temperature dependence of the quantum oscillations in the spin density wave phase, which attenuate exponentially below 5 K, and a nearly quadratic field dependence of the resistance in the lower field, high temperature metallic phase of the system. Some evidence is also present for additional sub-phase structure in the B-T phase diagram, but further work will be needed to make accurate assignments to these features. This work should serve as a guide to future investigations of the magnetic field dependent mechanisms and properties of quasi-one dimensional metals.

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## FIGURE CAPTIONS

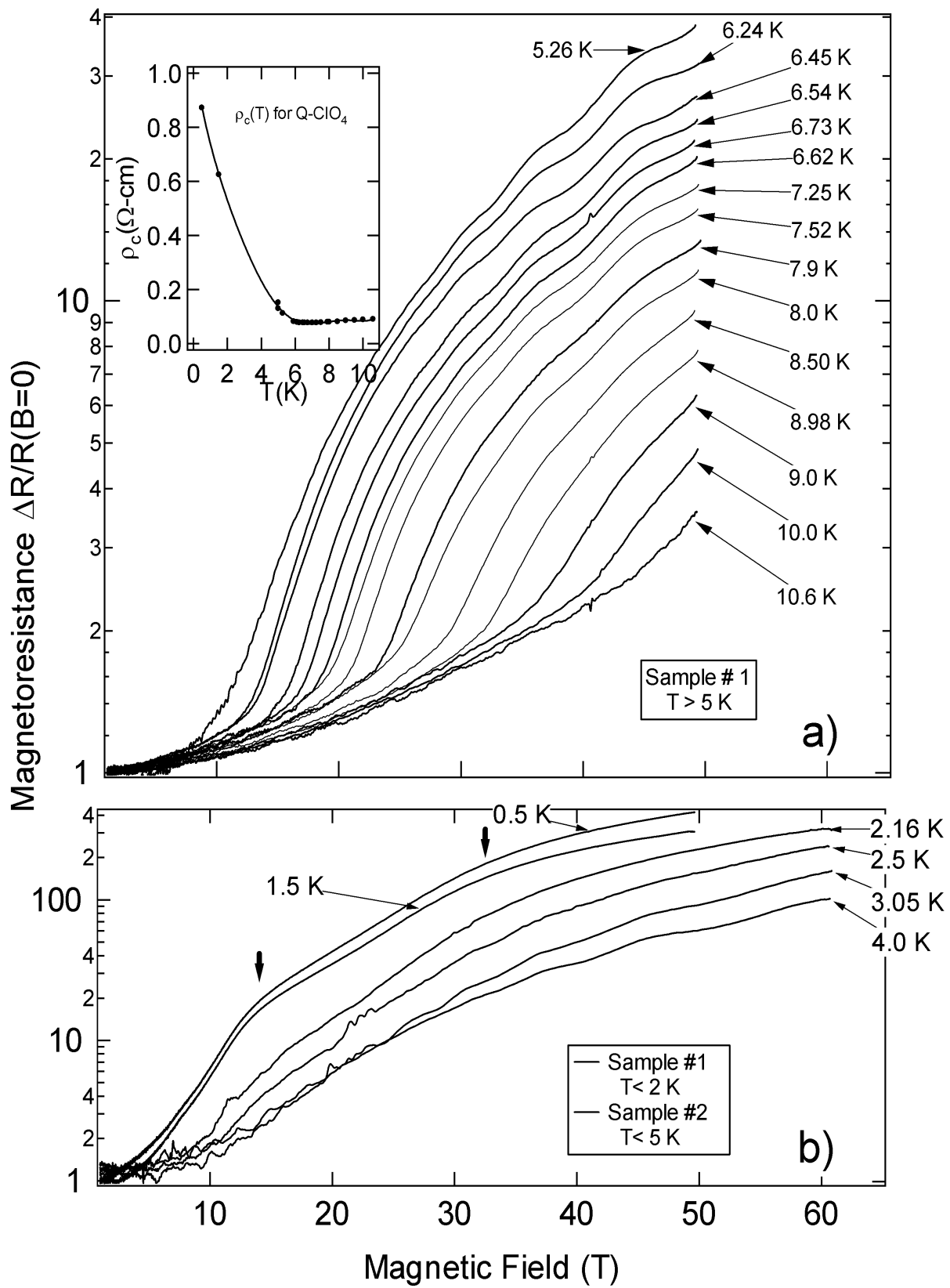
**Figure 1.** a) Magnetoresistance  $\Delta R/R(B=0)$  of thermally quenched  $(\text{TMTSF})_2\text{ClO}_4$  vs. pulsed magnetic field above 5 K (sample #1). Inset: zero field c-axis resistivity vs. temperature. b) Low temperature magnetoresistance vs. pulsed magnetic field for sample #1 and #2. Arrows indicate the position of structure in the lowest temperature data (see text).

**Figure 2.** Detail of the resistance of sample #1 vs. the square of the magnetic field for different temperatures. The solid line is a fit of the high temperature (10.4 K) resistance to a quadratic field dependence.  $B_{SDW}$  ( $T_{SDW}$ ) is defined as the point of deviation of the resistance from a quadratic behavior in field (open circles), and  $B'_{SDW}$  ( $T'_{SDW}$ ) is a second change in the field dependence (see arrows) of the resistance at higher fields. (Complete temperature labels, left to right, are 5.5, 6.45, 6.5, 6.54, 7.25, 7.52, 7.90, 8.5, 8.98, 9.0, 10.0, and 10.6 K.)

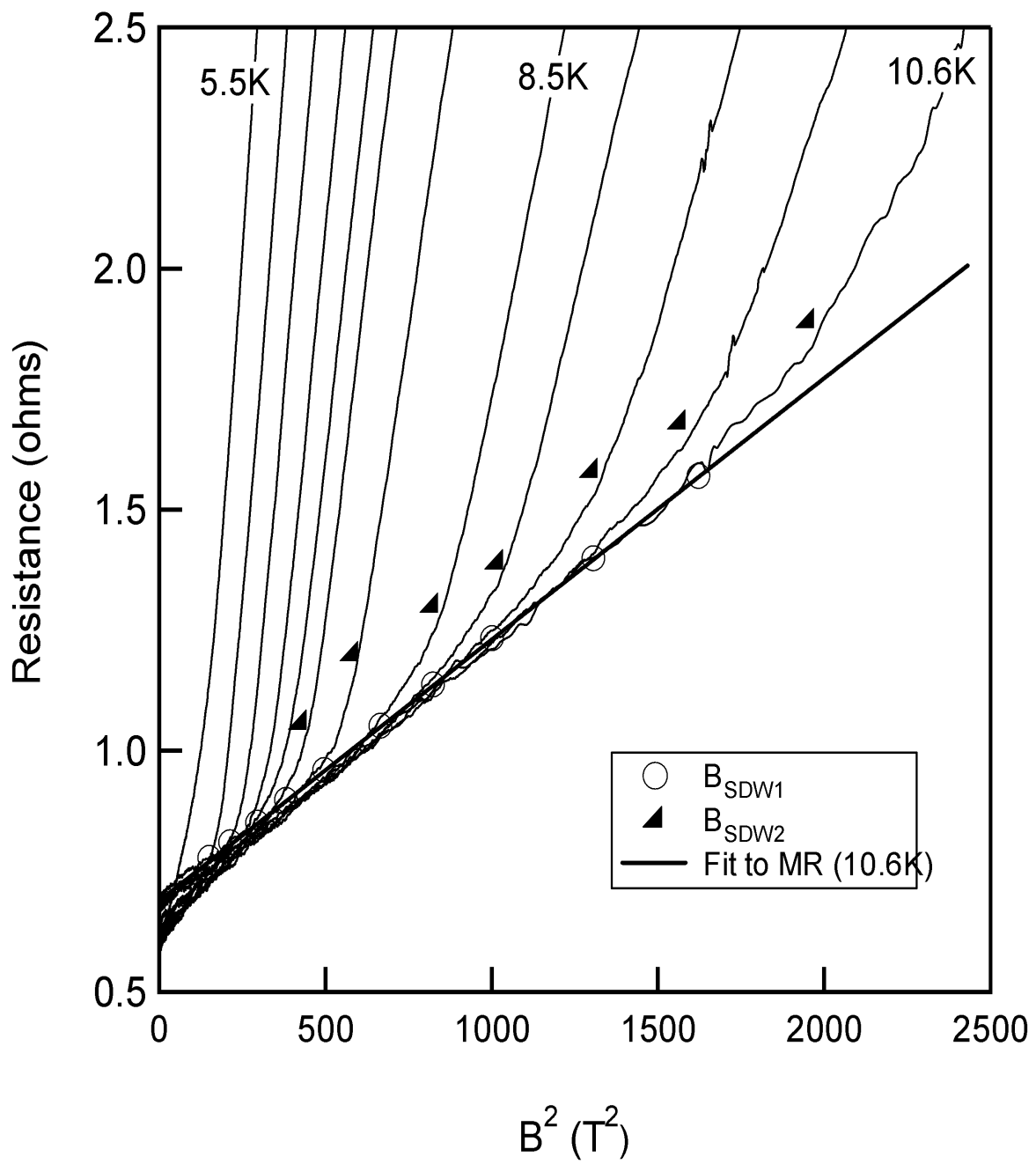
**Figure 3.** Temperature vs. magnetic field phase diagram of  $\text{Q-ClO}_4$  based on the values of  $T_{SDW}$  vs.  $B_{SDW}$  (also  $T'_{SDW}$  vs.  $B'_{SDW}$ ) obtained from Fig. 2. The solid lines are fits of the theoretical expression of Bjelis and Maki from Eq.1 with the parameters  $v_F$ ,  $T_0$ , and  $\varepsilon_0$  for  $\text{X} = \text{AsF}_6$  ( $v_F = 2.4 \times 10^5$  m/s;  $\varepsilon_0 = 7$  K;  $T_0 = 11.5$  K),  $\text{X} = \text{NO}_3$  ( $v_F = 2.4 \times 10^5$  m/s;  $\varepsilon_0 = 13$  K;  $T_0 = 11.0$  K), and  $\text{X} = \text{Q-ClO}_4$  ( $v_F = 1.1 \times 10^5$  m/s;  $\varepsilon_0 = 22.5$  K;  $T_0 = 13.0$  K). The dashed line is a polynomial fit to  $T'_{SDW}$  vs.  $B'_{SDW}$ . The lower phase diagram is for  $\text{R-ClO}_4$  after Ref.<sup>5</sup>. The finely dashed line is the main second order phase boundary between the metallic and FISDW phases. The other two phase lines  $T_H$  and  $T_R$  delineate sub-phases (See Ref.<sup>5</sup>.)

**Figure 4.** Temperature dependence of the quantum oscillations (normalized by the background magnetoresistance). The frequency is  $190 \pm 5$  T. a) Low temperature behavior (sample #2) below 5 K. b) High temperature behavior (sample #1) above 5 K. c) Plot of the amplitudes vs. temperature in the range 30 to 50 T for both samples measured. The

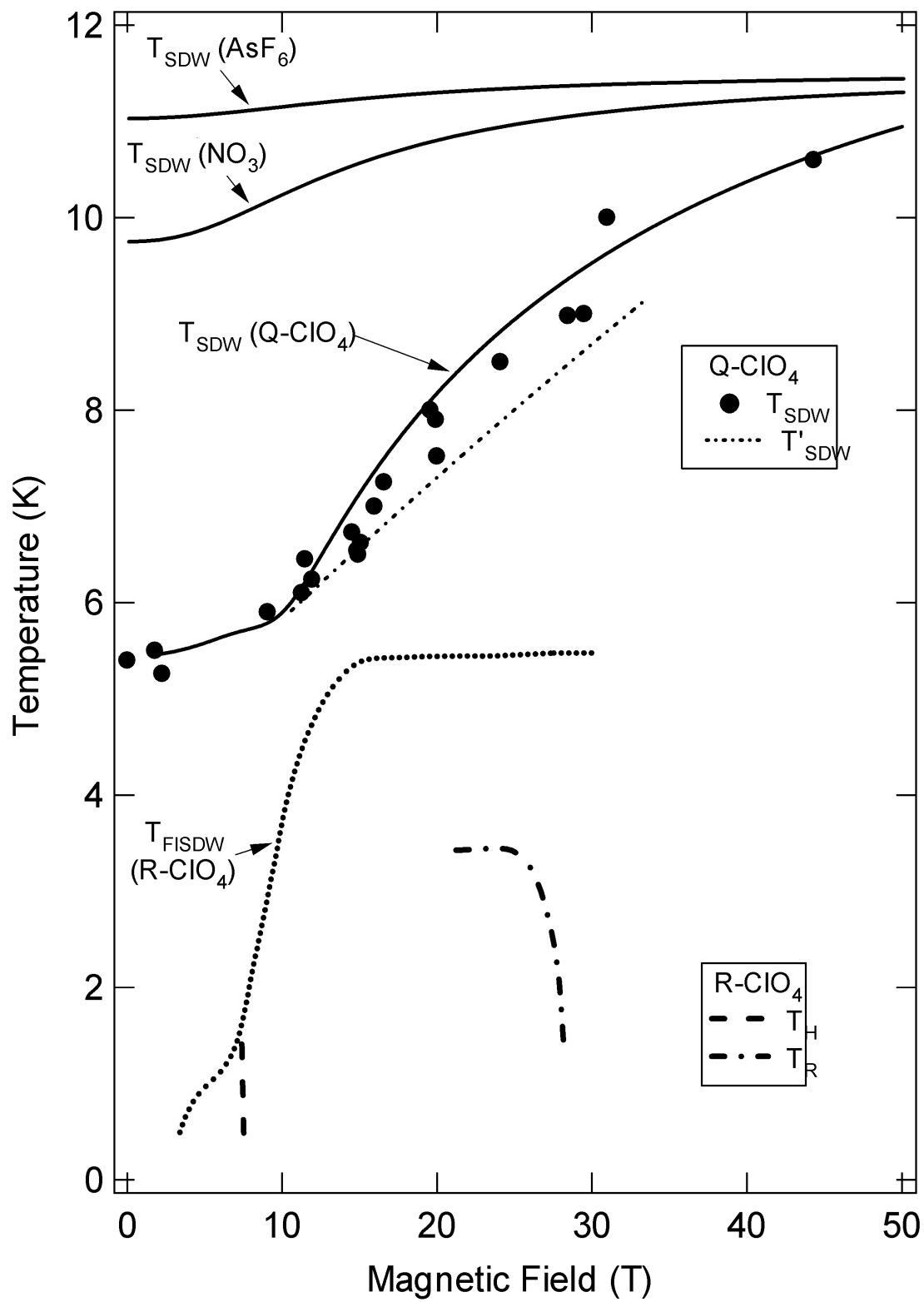
solid line is a fit to a modified version of the standard Lifshitz-Kosevich formula for quantum oscillation amplitudes in metals (see text).



Qualls et al., Fig. 1



Qualls et al. Fig. 2



Qualls et al., Figure 3

